Fabrication of Uranium Oxide Fuels

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ATR User Week 2012

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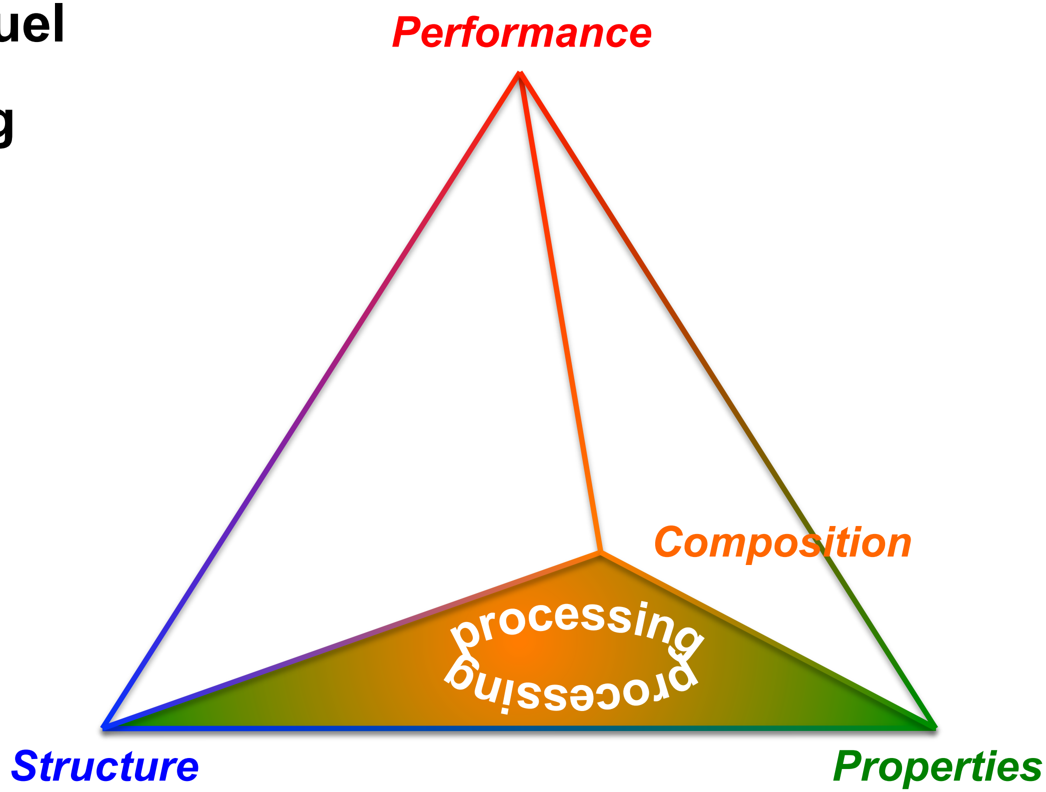
Outline

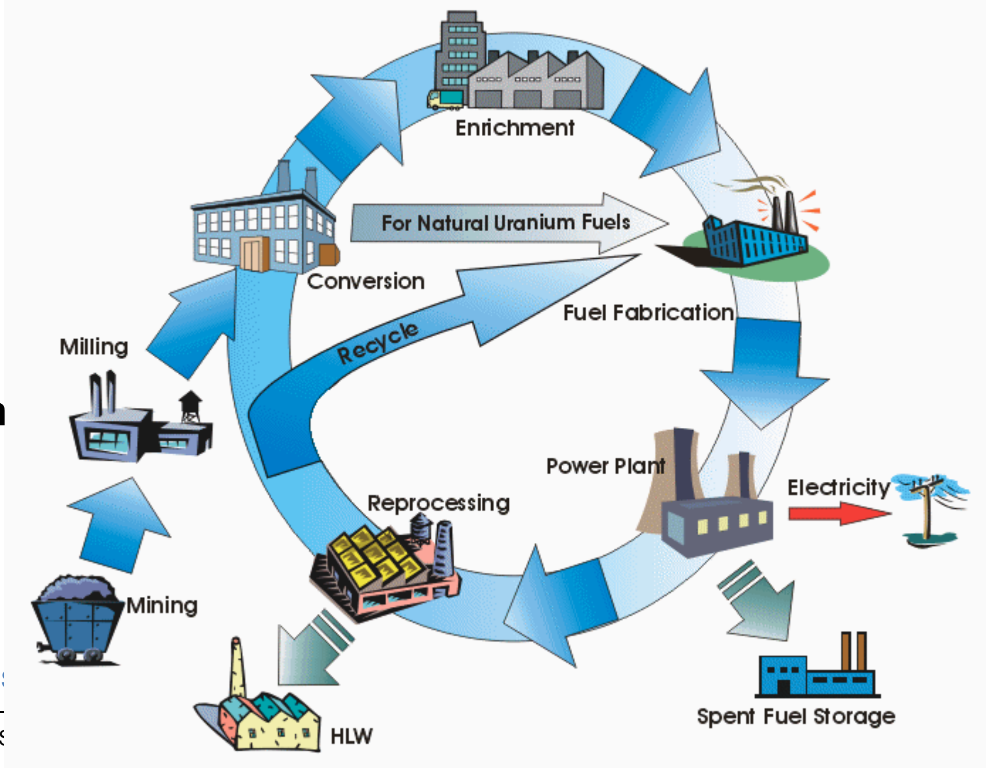
- **Ceramic Nuclear Fuel**
- **Powder Processing Science**
  - Powder feedstock
  - Compaction
  - Sintering
- **Summary**



MICROSTRUCTURE; e.g., grain size and porosity, AFFECTS PROPERTIES; e.g., thermal conductivity and creep

Uranium Fuel Cycle

- Exploration for uranium
- Mining and milling of uranium ore to produce uranium concentrate known as 'yellow cake'
- Purification and conversion of yellow cake into gaseous uranium hexafluoride (UF_6) suitable for enrichment to increase the proportion of 235U to 2-5%
- Conversion of enriched UF_6 to UO_2 powder suitable for making oxide fuel pellets
- Fabrication of uranium dioxide fuel pellets
- Fabrication of fuel pins made from stacks of UO_2 fuel pellets encapsulated in cladding, grouped in clusters, termed fuel assemblies
- Service
- Used fuel storage – recycle?



World LWR fuel fabrication capacity, metric tons/yr

Countries	Fabricator	Location	Conversion	Pelletizing	Rod/assembly
Belgium	AREVA NP-FBFC	Dessel	0	700	700
Brazil	INB	Resende	160	160	280
China	CNNC	Yibin	400	400	450
France	AREVA NP-FBFC	Romans	1800	1400	1400
Germany	AREVA NP-ANF	Lingen	800	650	650
India	DAE Nuclear Fuel Complex	Hyderabad	48	48	48
Japan	NFI (PWR)	Kumatori	0	360	284
	NFI (BWR)	Tokai-Mura	0	250	250
	Mitsubishi Nuclear Fuel	Tokai-Mura	475	440	440
	GNF-J	Kurihama	0	750	750
Kazakhstan	Ulba	Ust Kamenogorsk	2000	2000	0
Korea	KNFC	Daejeon	600	600	600
Russia	TVEL-MSZ*	Elektrostal	1450	1200	120
	TVEL-NCCP	Novosibirsk	250	200	400
Spain	ENUSA	Juzbado	0	300	300
Sweden	Westinghouse AB	Västeras	600	600	600
UK	Westinghouse**	Springfields	950	600	860
USA	AREVA Inc	Richland	1200	1200	1200
	Global NF	Wilmington	1200	1200	750
	Westinghouse	Columbia	1500	1500	1500
Total			**13433**	**14558**	**12662**

World Nuclear Association 2011

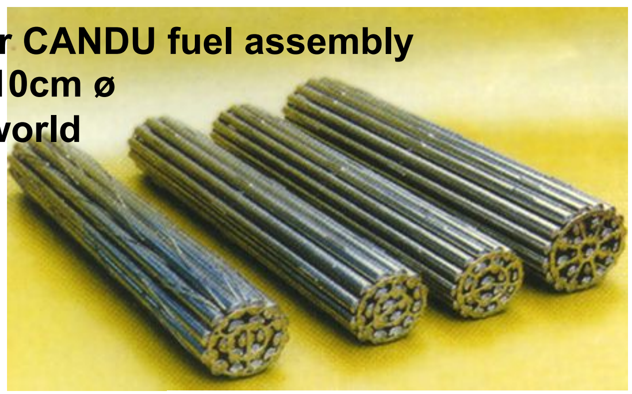
Types of Nuclear Fuel Assemblies

- Numerous fuel assembly types
- UO_2 pellets clad with zircalloy or stainless
- ~27 tons of fuel is required each year by a 1000 MWe reactor

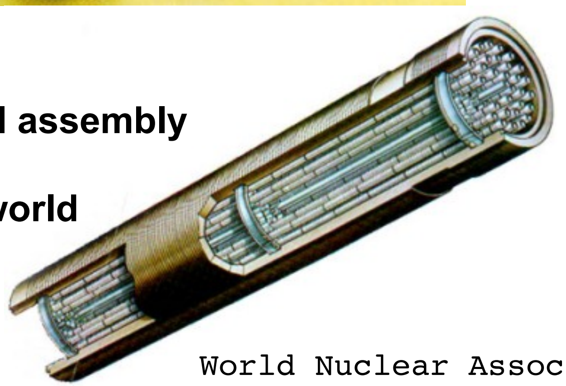
PWR fuel assembly
17x17
~4 meters
~66% of world capacity

BWR fuel assembly
6x6 to 10x10
~22% of world capacity

PHWR or CANDU fuel assembly
50cm x 10cm ø
~6% of world capacity



AGR fuel assembly
36 pin
~2% of world capacity

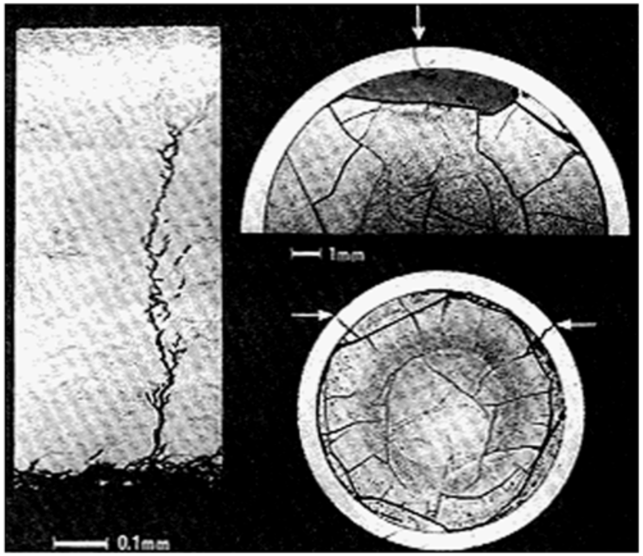


World Nuclear Association 2011

Ceramic Nuclear Fuel

- **Specifications based on 40+ years of experience**
  - Chemistry
  - Geometry
  - Microstructure
  - Physical
- **Fuel assemblies still fail due to pellet failure**
- **Science**
  - Separate effects of thermal gradients, radiation, microstructure etc. on thermal diffusivity, fission product distribution, pore generation and migration
  - Safer fuels – better scientific understanding
- **Other fuels**
  - Fast reactors
  - MOX, MA-MOX, thoria?
  - UN, UC, composites, targets?
  - Recycle?

Garzarolli et al., 1979



Fuel Failure – so what?

- High temperature, chemical corrosion, radiation damage, physical stresses
- Cladding is breached – radioactive material leaks into coolant water
- Not a significant plant safety risk
- “Very minor” leak – ignored leaking rod is removed at next refueling
- “Small” leak – allowable thermal transients are restricted
- “Significant” leak – reactor shutdown, faulty assembly removed
- Cost penalty to operating at reduced power or shutdown & replace failed fuel with matching remaining enrichment
- Balance economics and longer fuel burn

Bottom line: pellet failure affects the bottom line

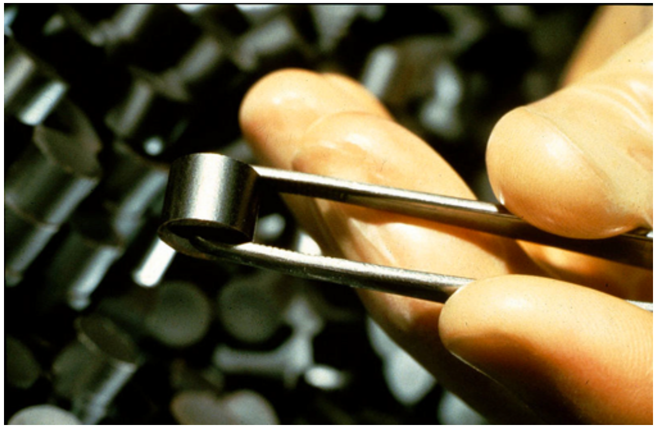
Minimizing fuel failure

- **Fuel failure rates improved ~ 60% from 1986 to 2006**
- **~14 leaks per million rods loaded (IAEA 2010)**
- **Exclusion of foreign material from primary coolant water**
  - Sophisticated debris filters
- **Improved cleanliness in fuel assembly**
- **Pellet – Clad Interaction (PCI)**
  - Power transients
  - PCMI: Pellet – Clad contact pressure
  - PCCI: Chemical reaction – build up of e.g. iodine, cesium, cadmium
  - Fragmented "relocated" fuel pellets
  - Localized heating

Suspect missing pellet surface

Fuel Pellet Specifications

- **87.7% uranium**
- **Total impurities 1500µg/g**
- **O/M from 1.99 to 2.02**
- **Equivalent Boron Content (EBC) < 4.0 µg/g (B, Gd, Eu, Dy, SM, Cd)**
- **Dimensions TBD (diameter, length, perpendicularity, surface finish)**
  - ~1 cm x 1.2 cm (+/- ~0.001)
- **Density TBD**
  - 95% of theoretical – 10.96 g/cc
- **Grain size and pore morphology TBD**
  - ~30 µm
- **Pellet integrity**
  - Visually acceptable
- **Cracks**
  - ½ the pellet length, 1/3 the pellet circumference
- **Chips**
  - 1/3 of the pellet end
  - > 5% of cylindrical area

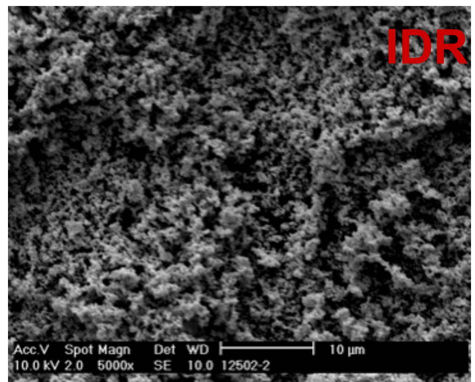


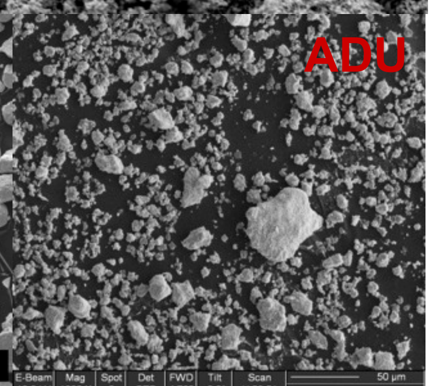
Fabrication of UO_2 Fuel Pellets

"Turning big rocks into little rocks then turning little rocks into big rocks"

- **Powder synthesis**
  - IDR (Integrated Dry Route)
  - ADU (Ammonium Diuranate)
  - AUC (Ammonium Uranium Carbonate)
- **Powder conditioning**
- **Compaction**
- **Thermal treatment**

Path Dependent





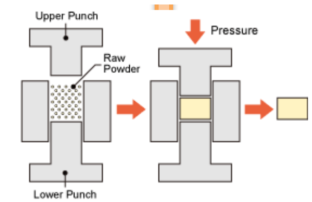
UO2 Powder | **Recycled Powder**

Additives
– binder, lubricant, poisons

Milling

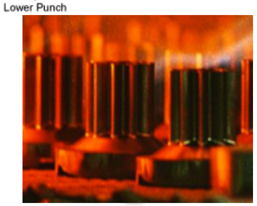
Sieving

Granulation



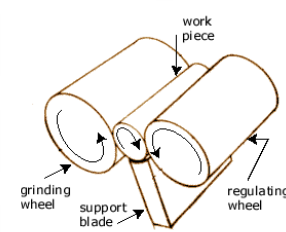
Pressing

Burnout



Sintering

Grinding

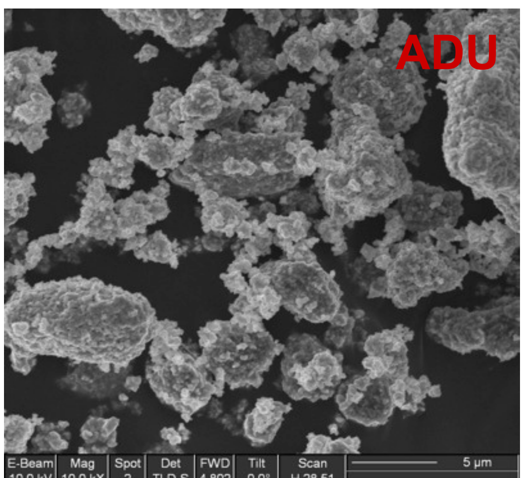


Inspection

Service

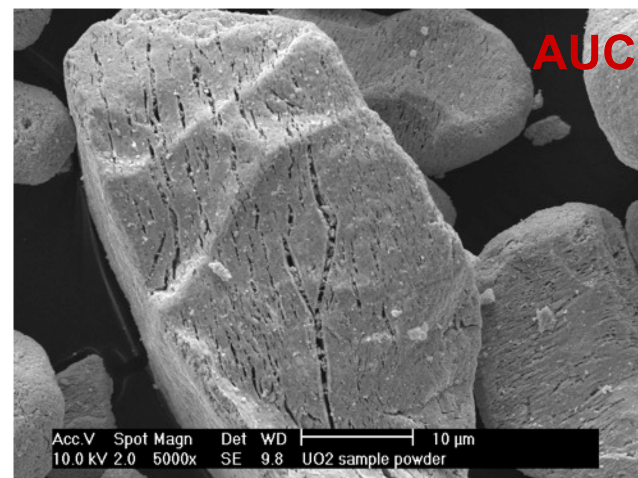
Black Art or Science?

- **Process knowledge is not directly transferrable**
  - Specifications for powder feedstock has limitations
  - Feedstock will change
  - Small changes to feedstocks will affect processing parameters
  - How do you compensate for variations?
- **Chemistry/powder additions for MOX, MA-MOX**
- **Material recycled from used fuel will come in many forms**

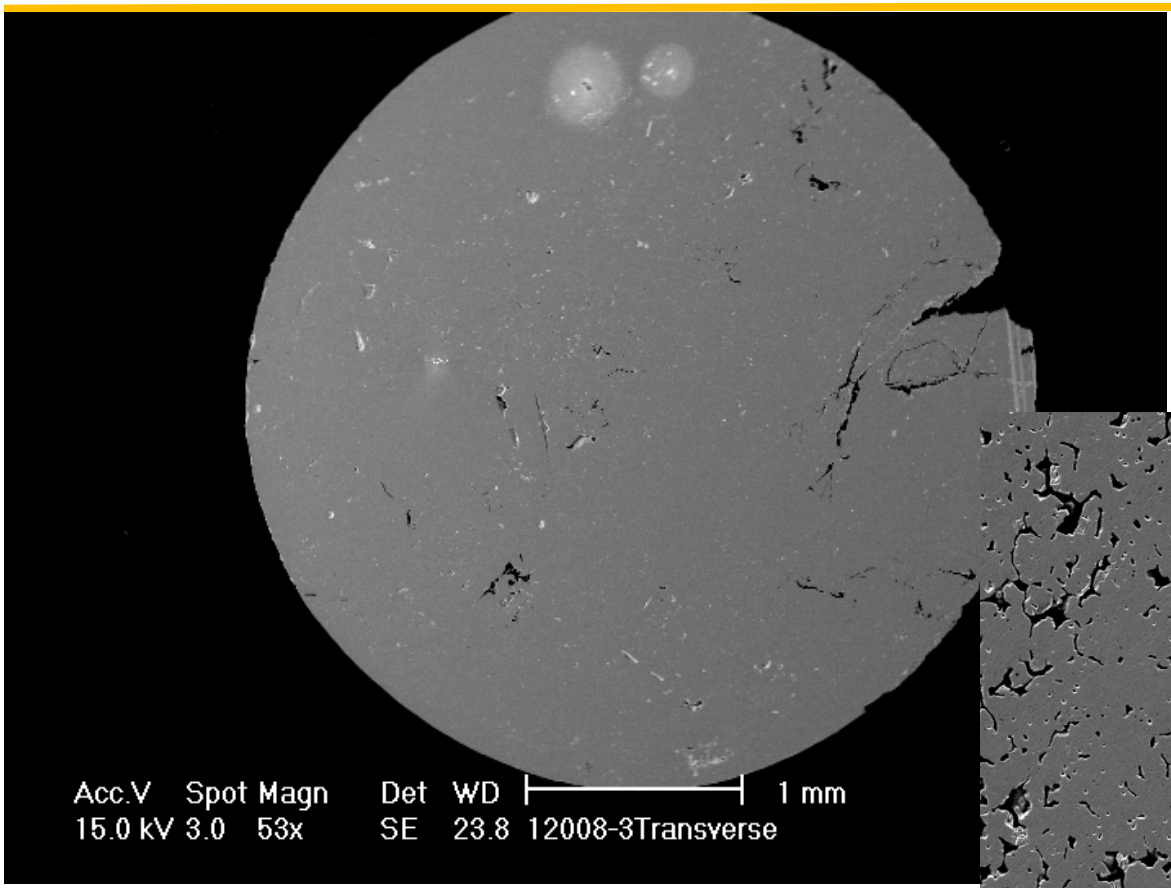


Would you treat this powder the same as this powder?

What would you do differently to get the same pellet?



The crime…



Porosity that will alter heat transfer and fission gas transport properties

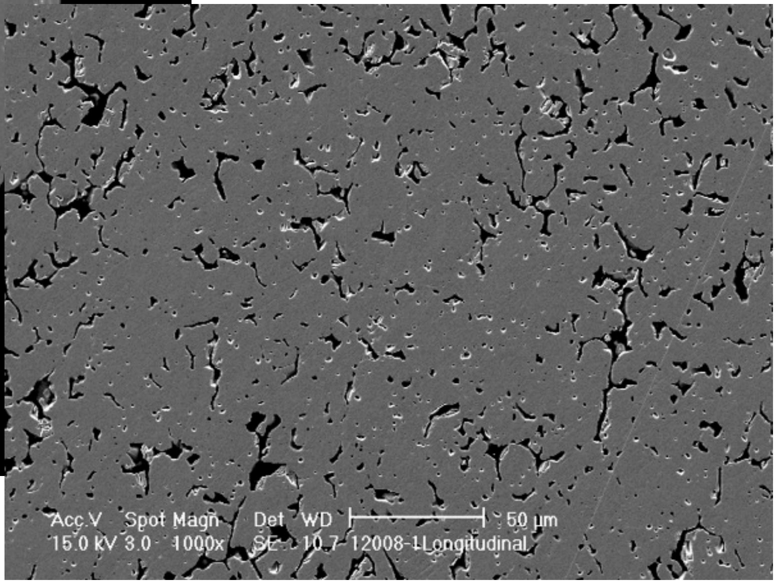
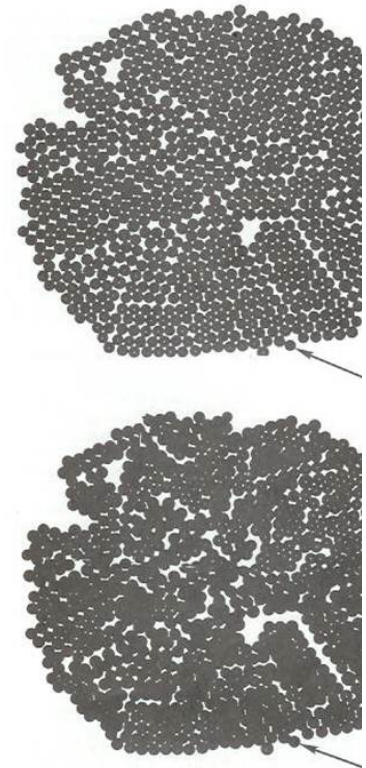


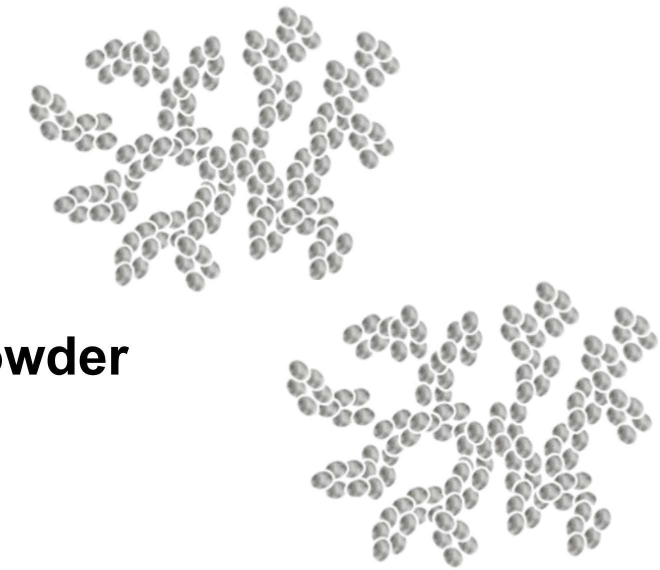
ABB DUO_2 sintered at 1750 ˚C

I suspect the powder…

- **UO_2 powder particle variables**
  - Morphology
  - Agglomeration
    - Hard
    - Soft
  - Size distribution
  - Powder flow into die
    - Uniformity
- **Solutions to some powder particle variables**
  - Milling
  - Sieving

Seemingly uniform packing

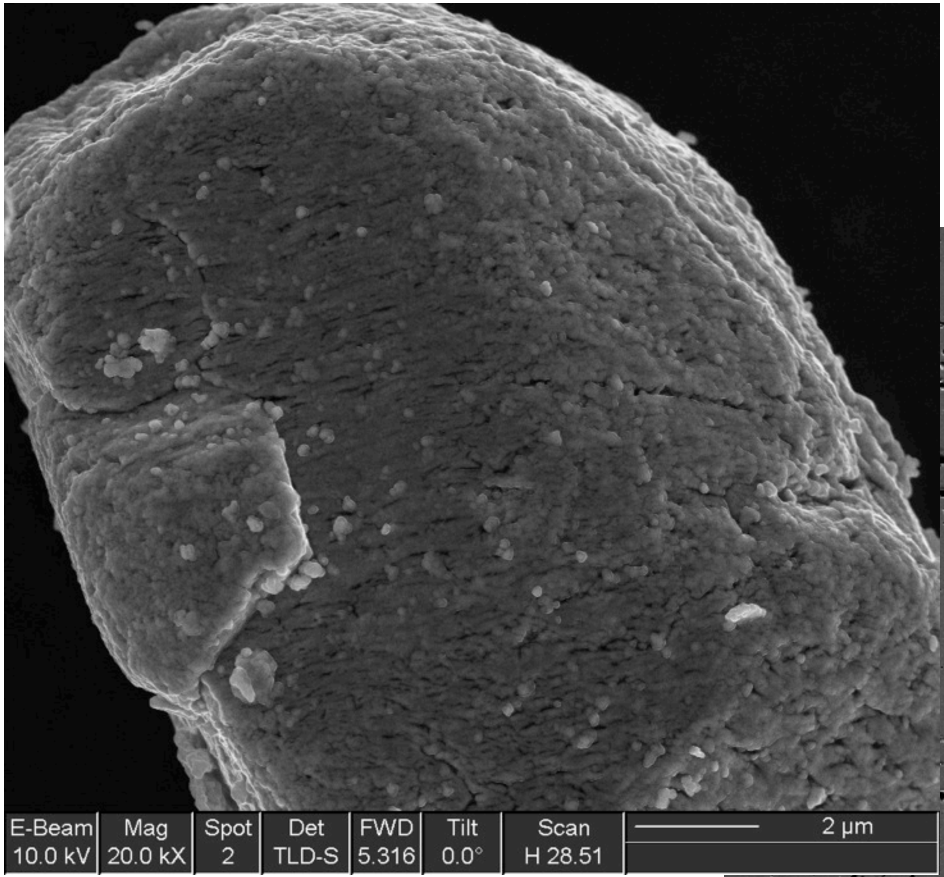




Particle agglomerates

E. Liniger & R. Raj

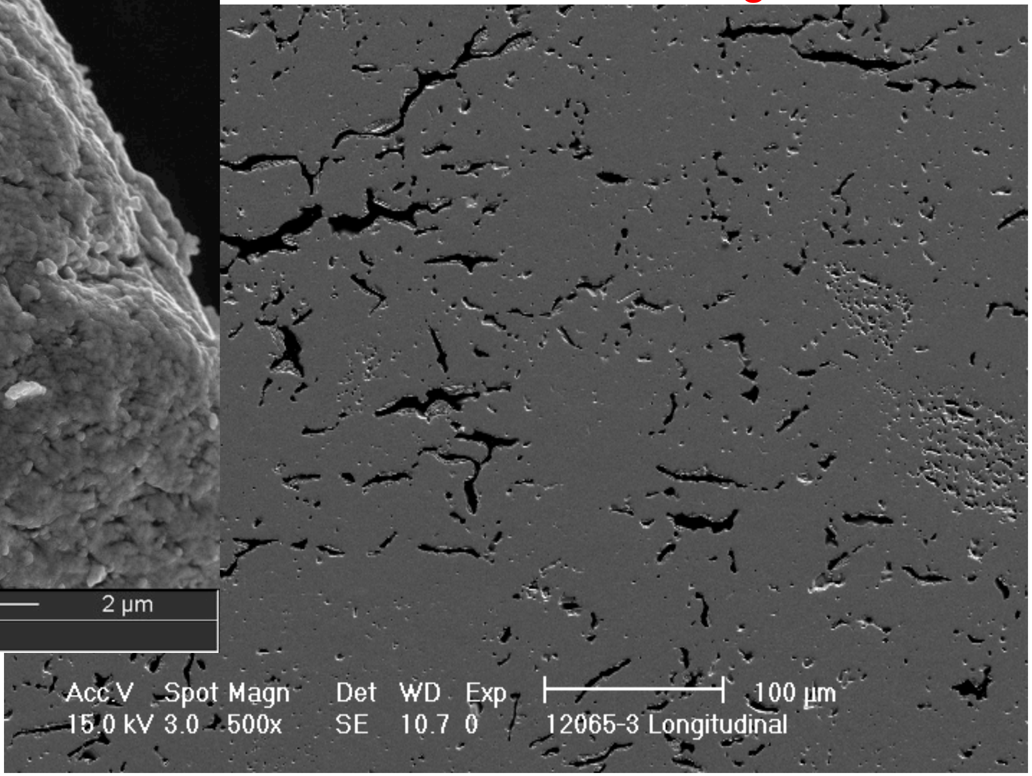
Guilty…



As-received powder

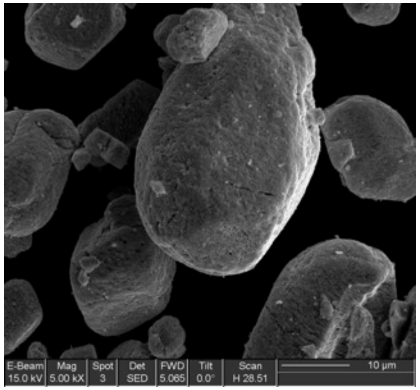
Poor Powder Flow & Microporosity

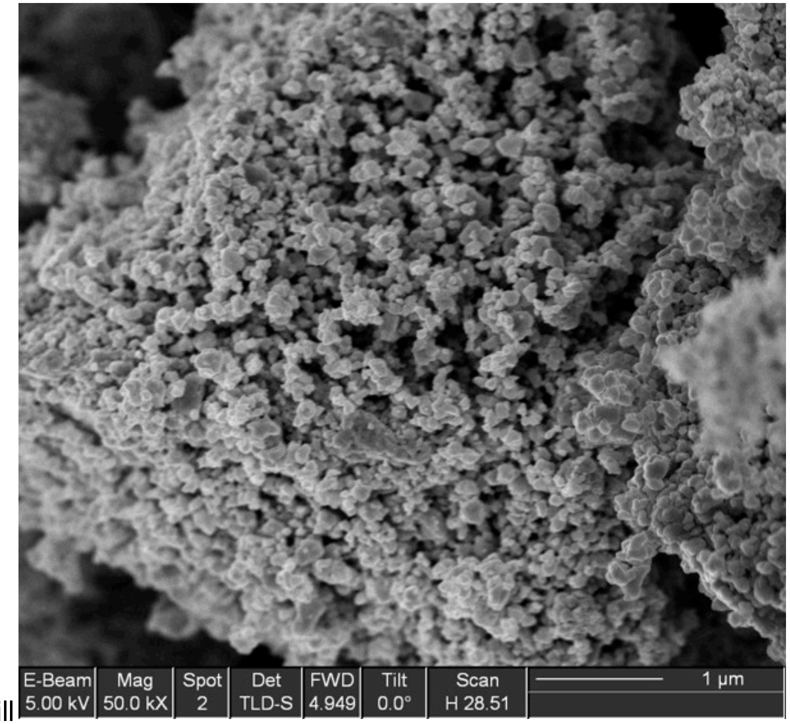
Isolated "stranded" pores affect sintering rate

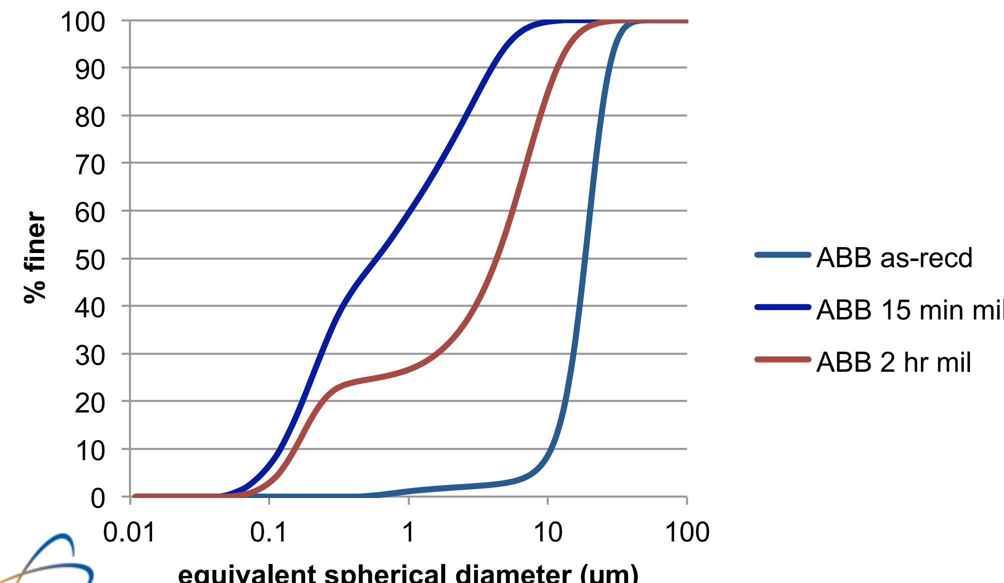


Pellet sintered at 1750 ˚C

Reforming the powder…





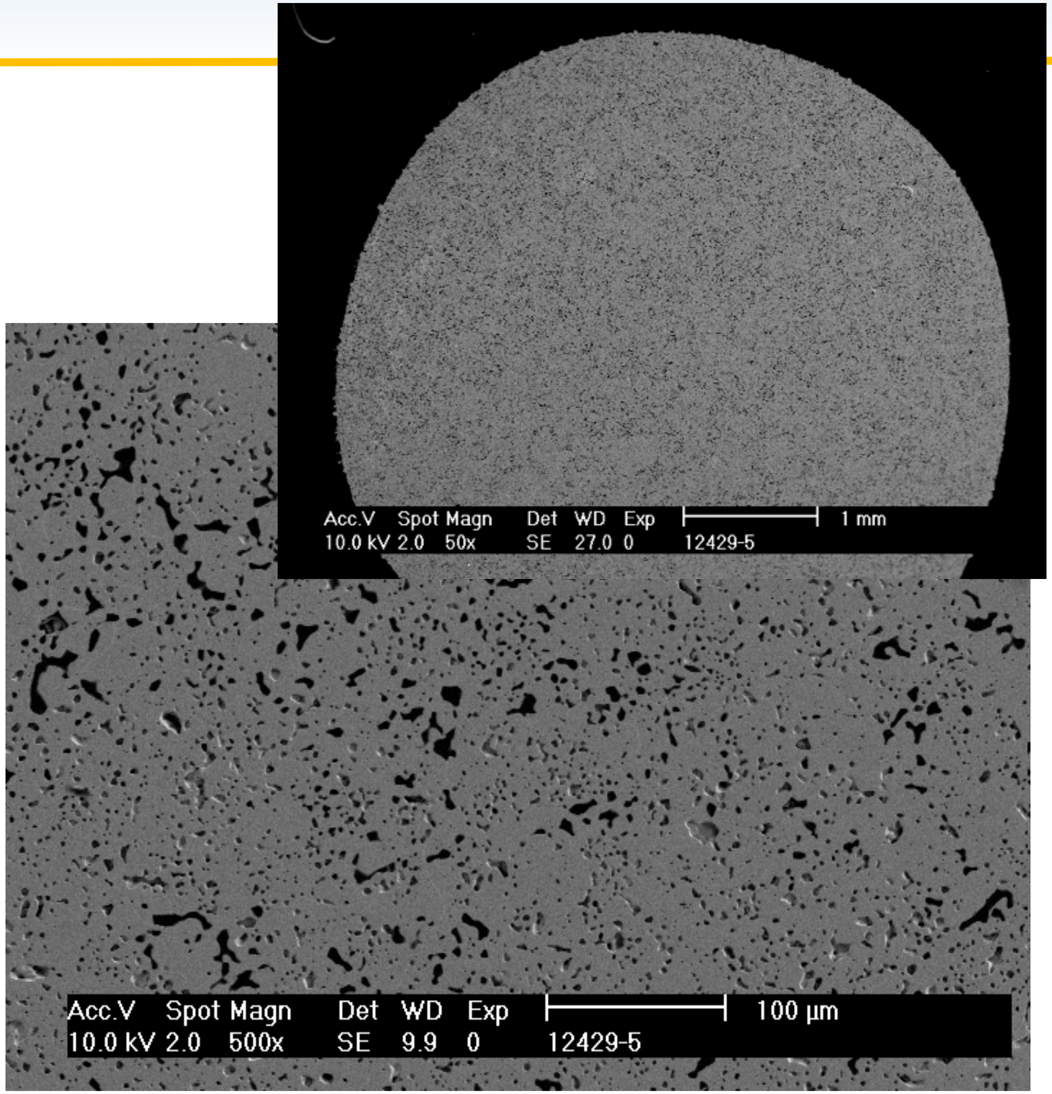


Surface area ABB
as-received: 5.5 m^2/g
2 hr milled: 7.3 m^2/g

A repeat offender…

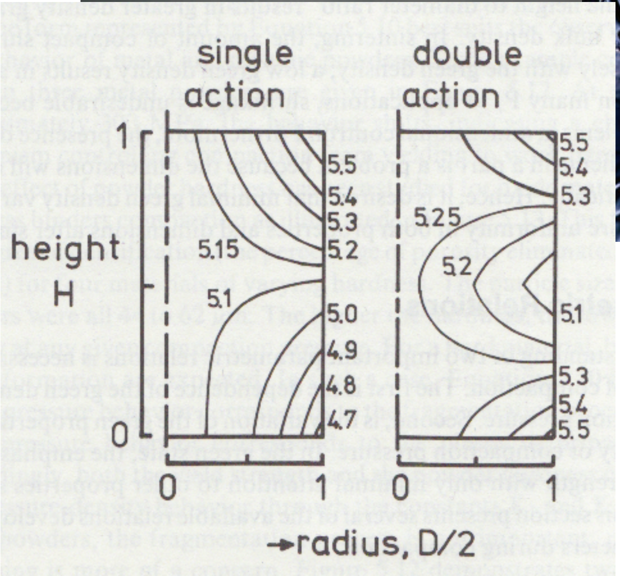
- **No cracking**
  - Die filling improved
  - Stresses reduced
- **Still porous**
  - Pore shape improved

Want higher density



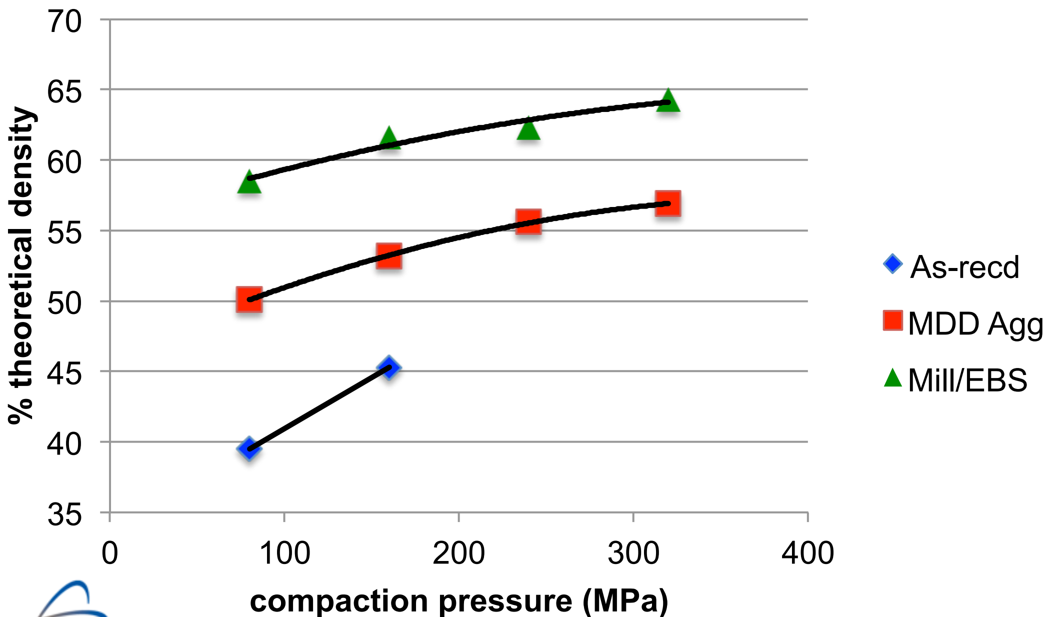
Digging deeper…

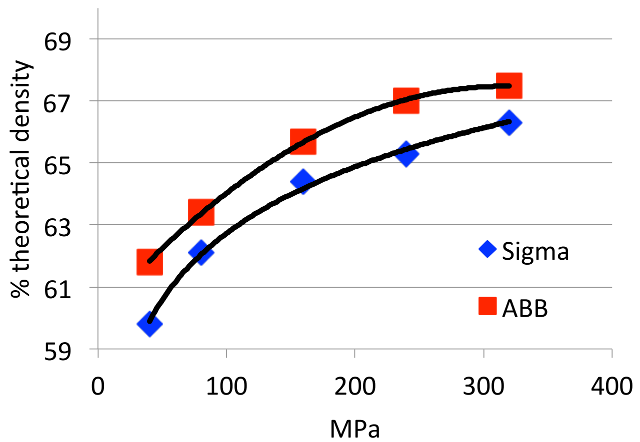
- **Compaction**
  - Air removal
  - Friction
    - Die wall
    - Powder/powder
- **Solutions**
  - Lubricants
    - Oil for tooling
    - Stearic acid
  - Tooling
    - e.g., carbide liners



Green density

- DUO_2 powder (various sources)
  - As received
  - Milled
  - Milled for 15 min with EBS
- Pellets pressed in dual action punch and die set
  - Nominal 5.7 mm diameter by 5 mm thick

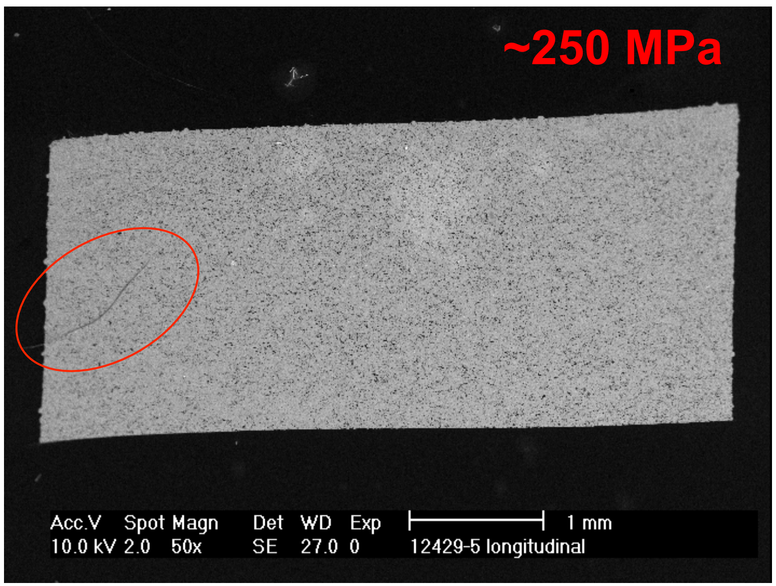


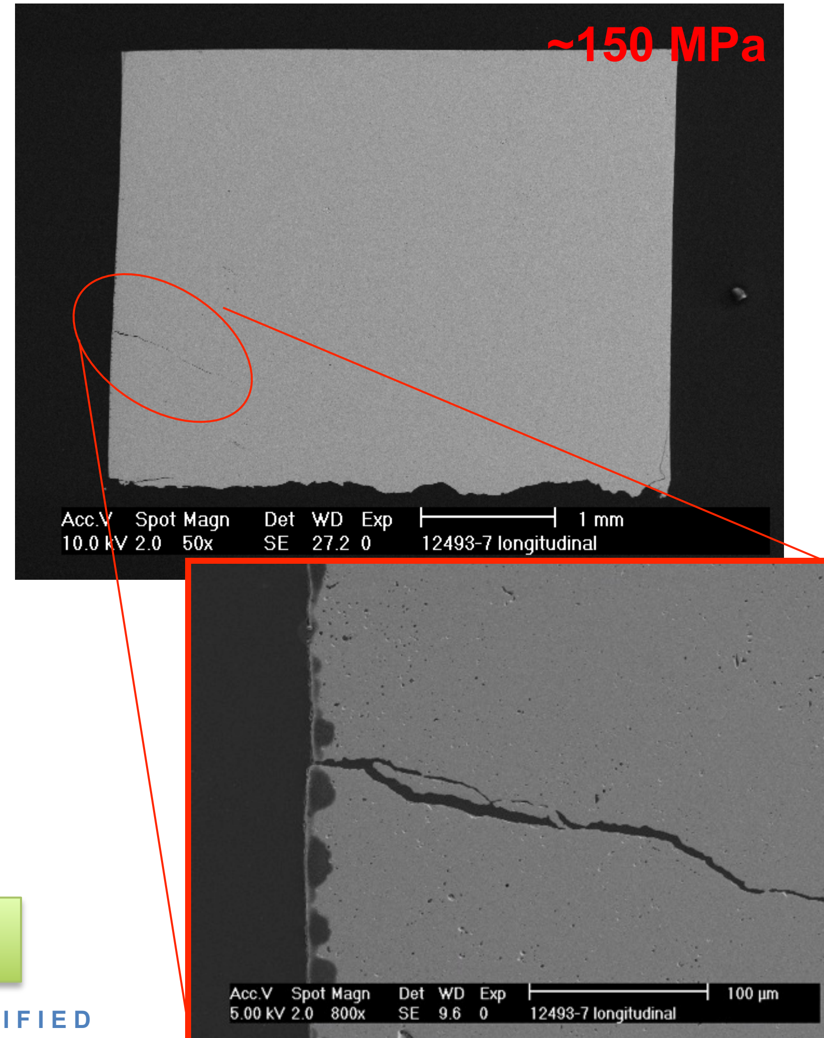


Volumetric *densities sensitive to O/M ratio*
Trend line added to aid eye

Pressure – enough is enough

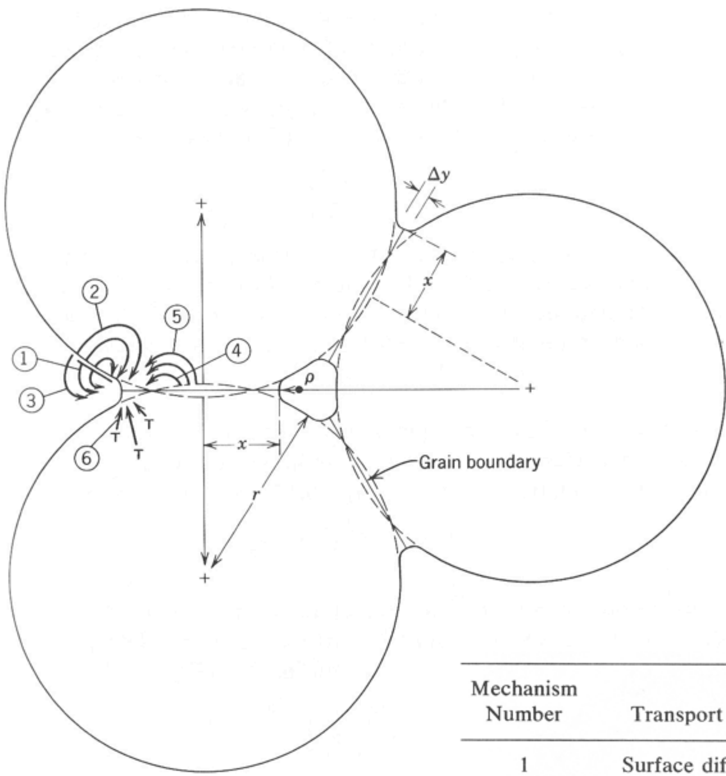
- **Delamination**
- **Cracks follow density gradients**
  - Higher gradient when thicker





Defects don’t go away

Sintering Theory



Sintering requires mass diffusion

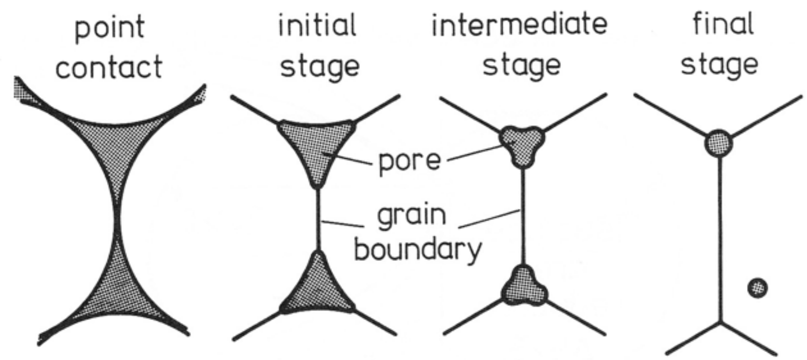
- Pore removal can be driven by chemical potential due to geometry
  - Surface area
  - Particle size
  - Chemical heterogeneity
  - Stoichiometry (O/M ratio)
  - Macroscopic heterogeneity
  - Microscopic heterogeneity
  - Heat transport

Mechanism Number	Transport Path	Source of Matter	Sink of Matter
1	Surface diffusion	Surface	Neck
2	Lattice diffusion	Surface	Neck
3	Vapor transport	Surface	Neck
4	Boundary diffusion	Grain boundary	Neck
5	Lattice diffusion	Grain boundary	Neck
6	Lattice diffusion	Dislocations	Neck

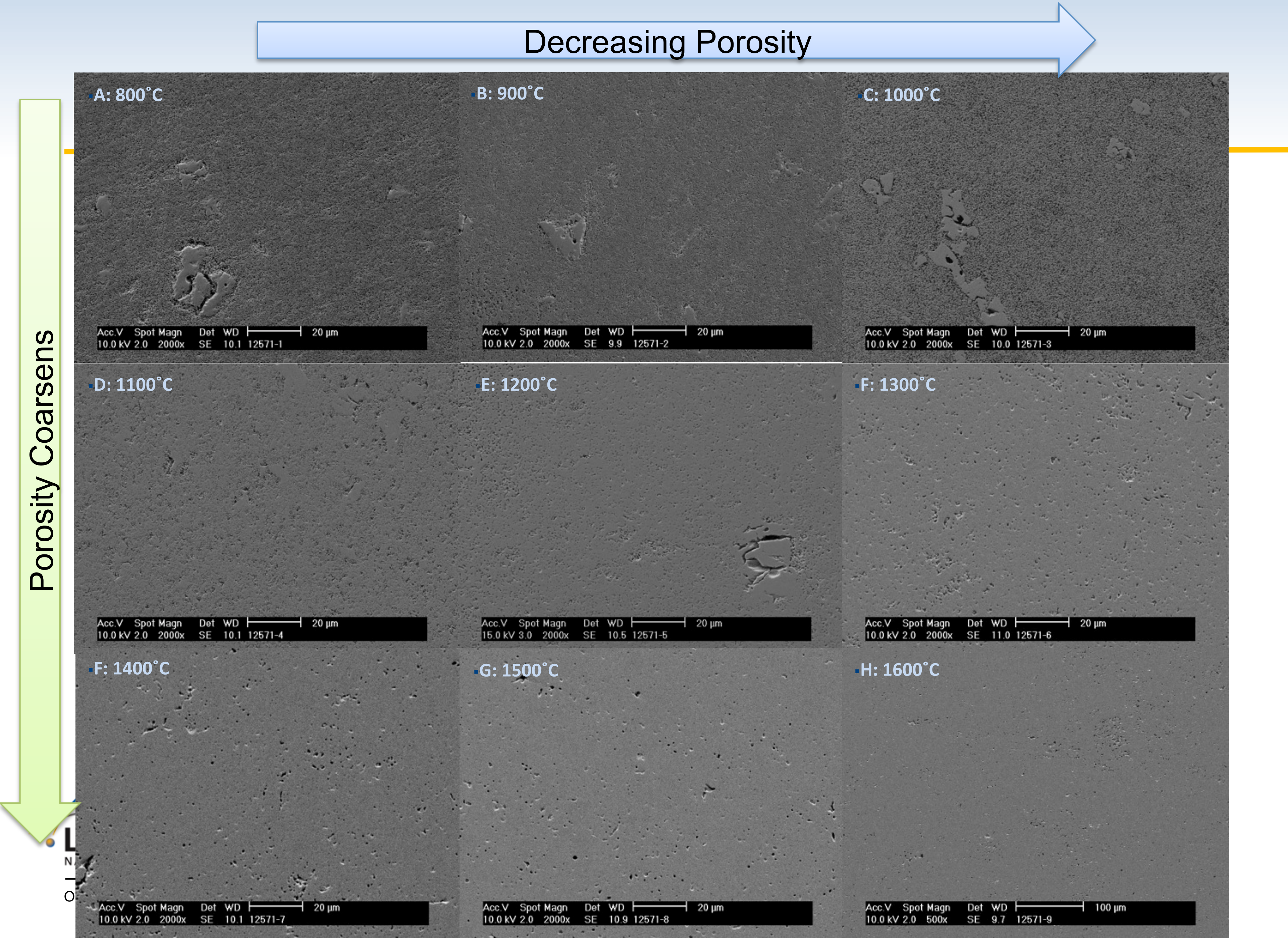
Introduction to Ceramics, W Kingery, H Bowen, D Uhlmann, John Wiley & Sons, 1976

Sintering Theory

- **Initial**
  - Surface smoothing
  - Grain boundaries/necks form
  - Rounding of open pores
- **Intermediate**
  - Pore shrinkage at boundaries
  - Mean porosity decreases
  - Slow grain growth
- **Final**
  - Closed pores
  - Pores at boundaries shrink or disappear
  - Large pores shrink slowly
  - Fast grain growth
  - Trapped pores shrink slowly



Powder Metallurgy Science, R. German, Metal Powder Industries Foundation, 1984

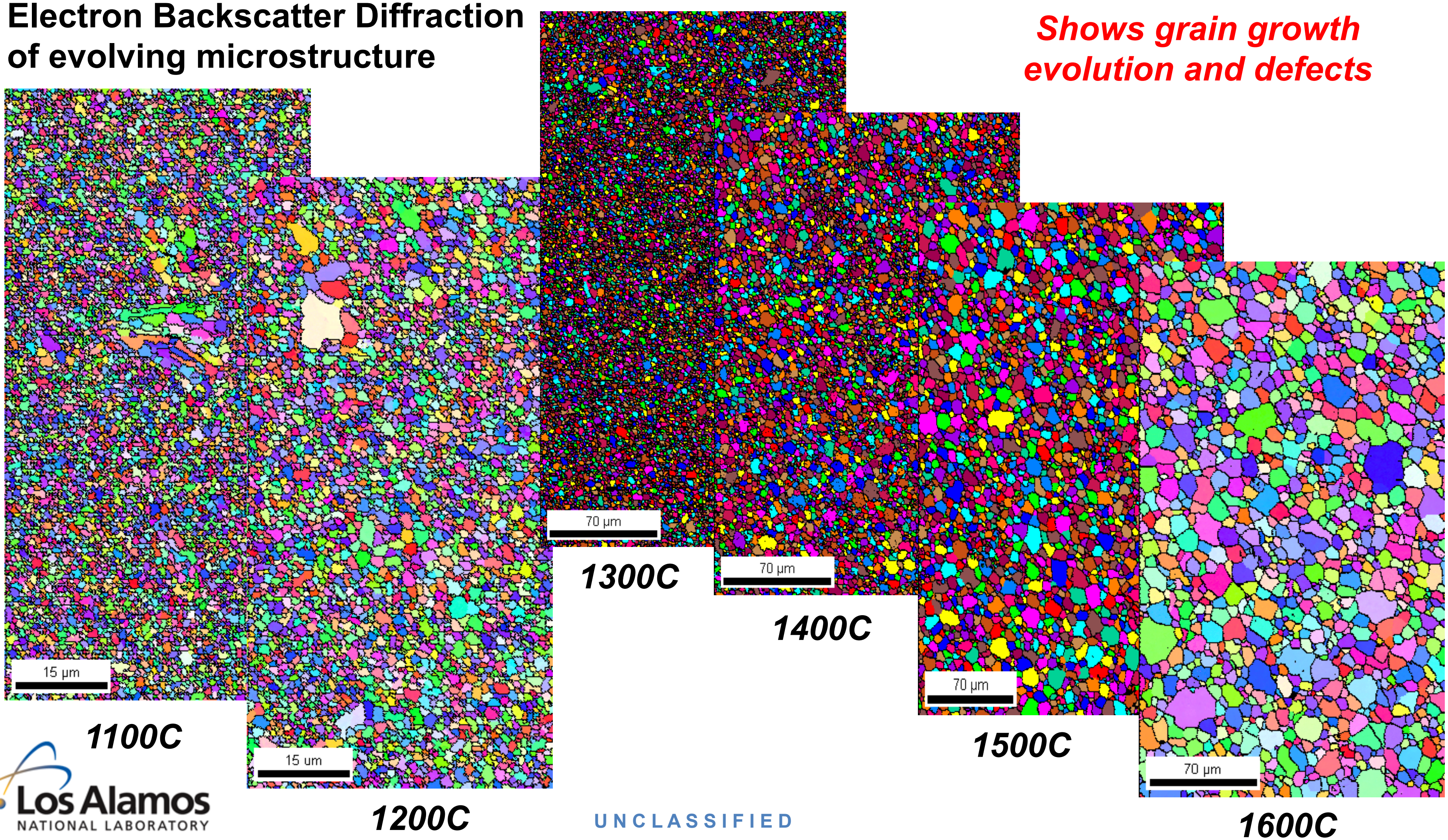


Decreasing Porosity
Porosity Coarsens
A: 800˚C
B: 900˚C
C: 1000˚C
D: 1100˚C
E: 1200˚C
F: 1300˚C
F: 1400˚C
G: 1500˚C
H: 1600˚C
Acc.V Spot Magn Det WD 20 µm
10.0 kV 2.0 2000x SE 10.1 12571-1
Acc.V Spot Magn Det WD 20 µm
10.0 kV 2.0 2000x SE 9.9 12571-2
Acc.V Spot Magn Det WD 20 µm
10.0 kV 2.0 2000x SE 10.0 12571-3
Acc.V Spot Magn Det WD 20 µm
10.0 kV 2.0 2000x SE 10.1 12571-4
Acc.V Spot Magn Det WD 20 µm
15.0 kV 3.0 2000x SE 10.5 12571-5
Acc.V Spot Magn Det WD 20 µm
10.0 kV 2.0 2000x SE 11.0 12571-6
Acc.V Spot Magn Det WD 20 µm
10.0 kV 2.0 2000x SE 10.1 12571-7
Acc.V Spot Magn Det WD 20 µm
10.0 kV 2.0 2000x SE 10.9 12571-8
Acc.V Spot Magn Det WD 100 µm
10.0 kV 2.0 500x SE 9.7 12571-9

Grain Evolution During Sintering

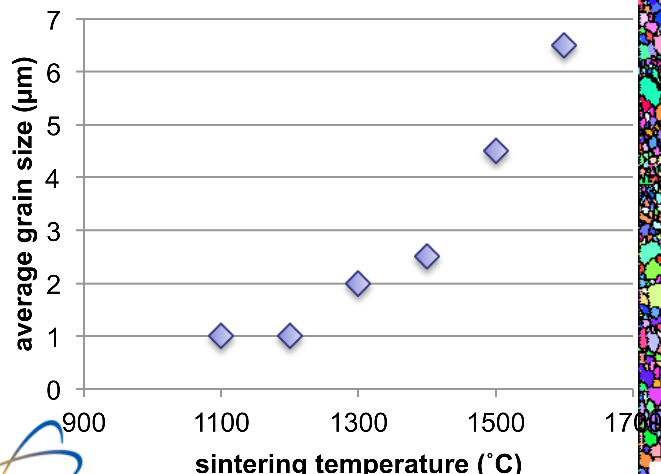
Electron Backscatter Diffraction of evolving microstructure

Shows grain growth evolution and defects

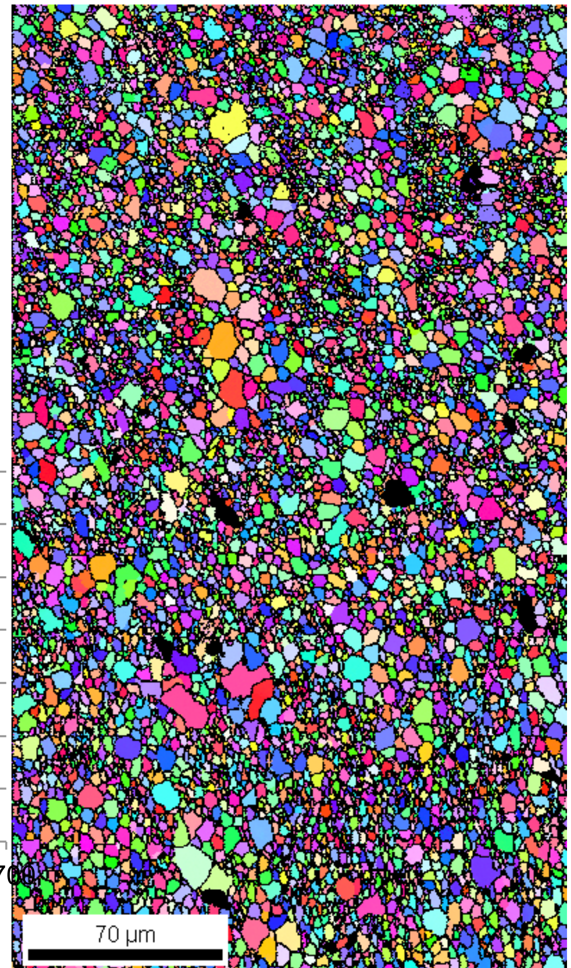


Grain size “control”

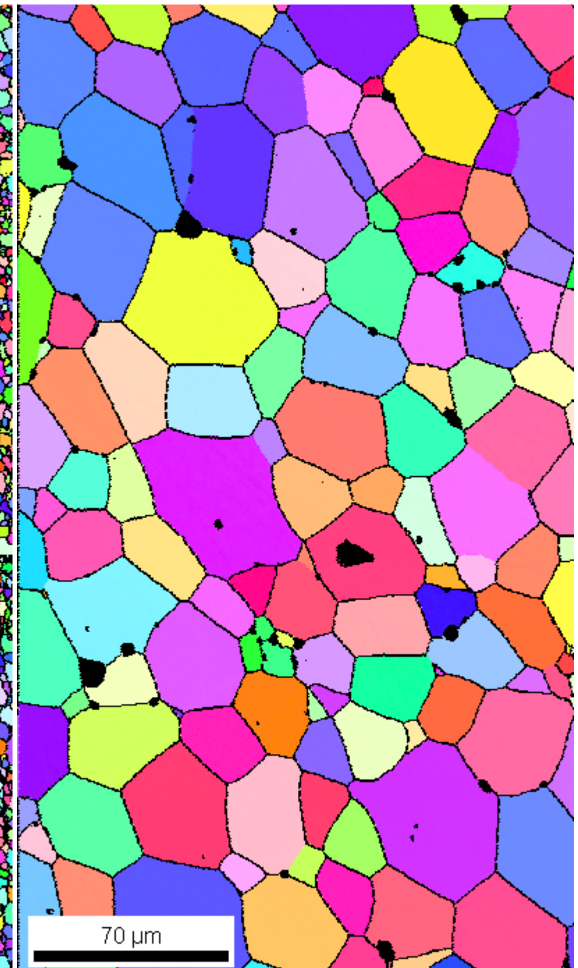
- EBSD images of pellets sintered under gettered argon
- Grains grown from 3 microns to 21 microns
- Density relatively constant 92% and 93% respectively
- No strong texture



1350˚C 4 hrs – 91.8%



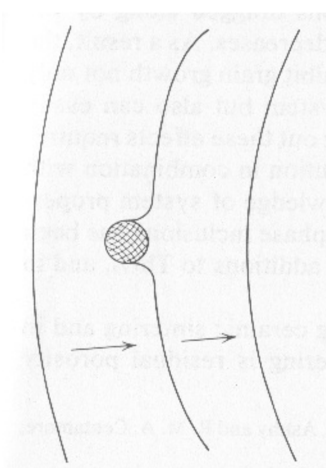
1650˚C 4 hrs – 93.4%



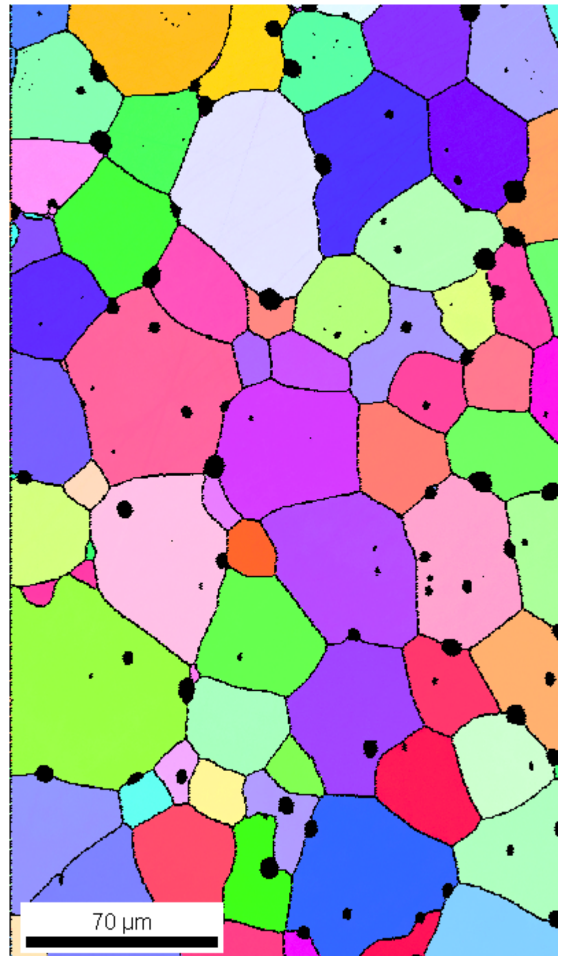
Grain size control

- Addition of aluminum from ADS (aluminum distearate) ~100 ppm
- Al_2O_3 is known to pin grain boundaries
- 1650˚C for 4 hrs
- Grain size decreased from 21 μm to 11 μm

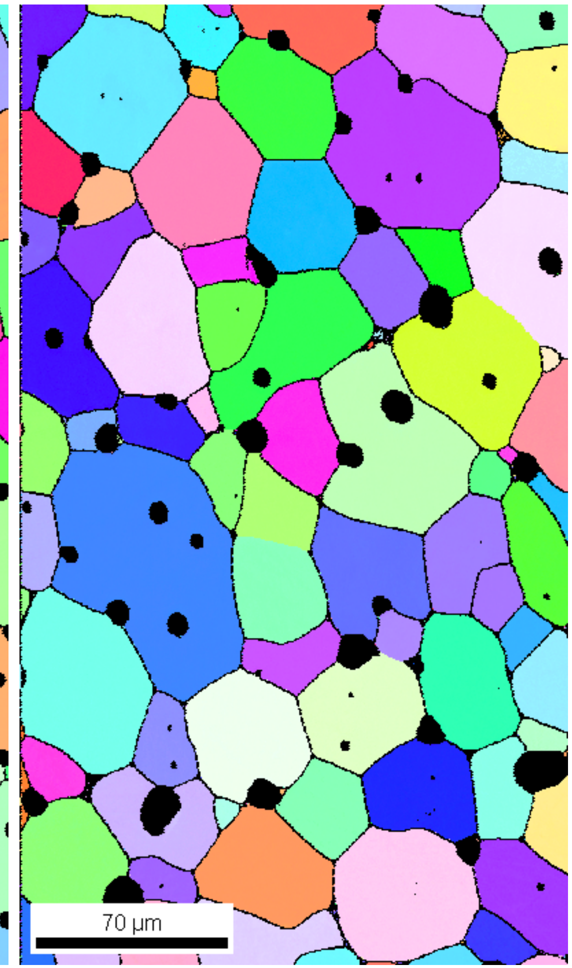
Minimizing grain boundary energy



As rec'd – 94.5%

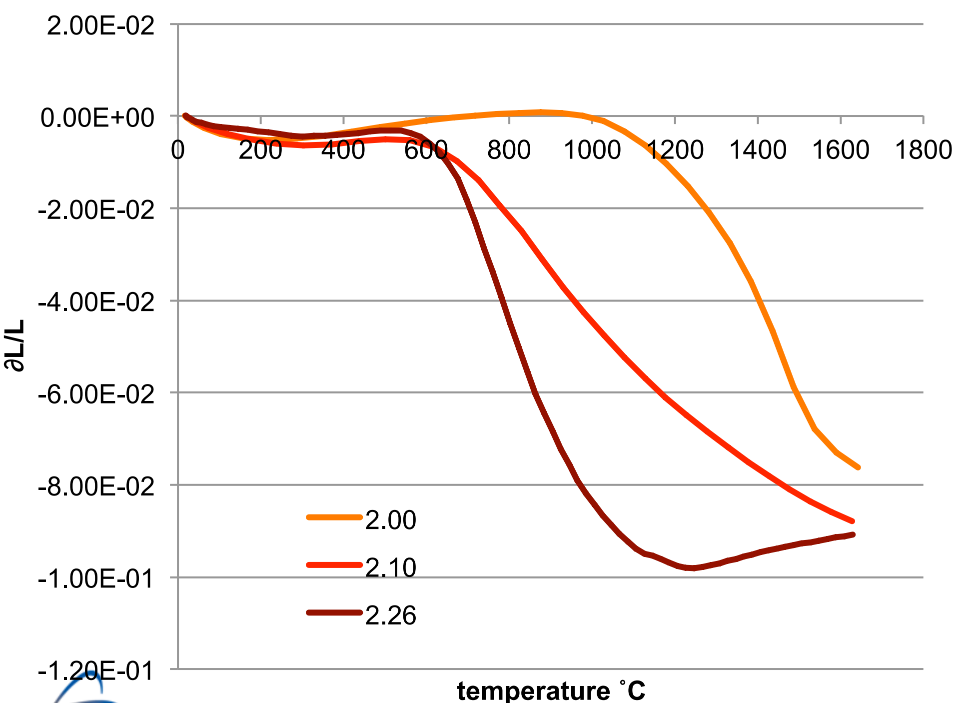


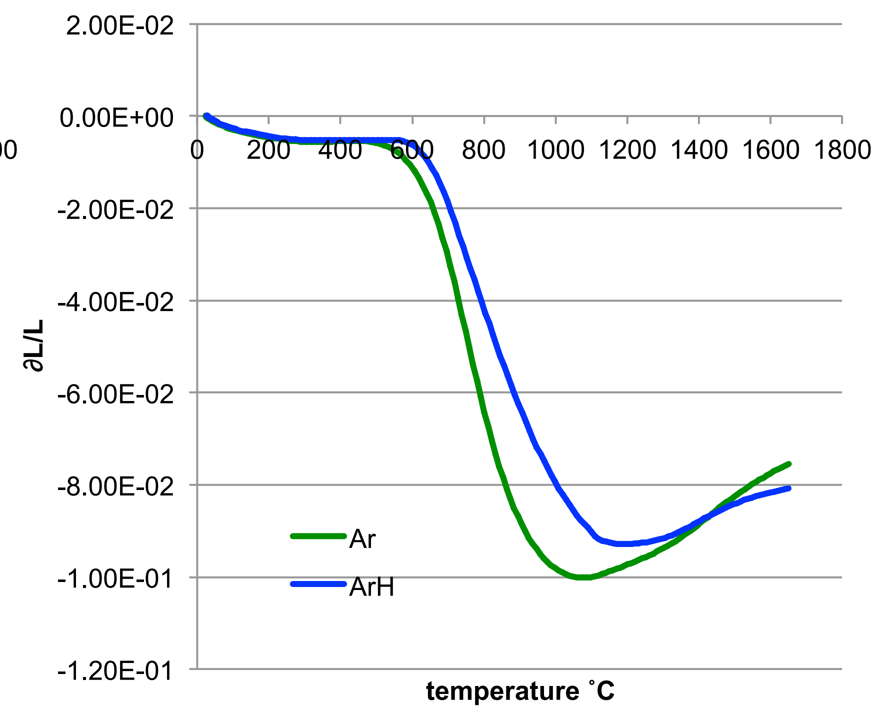
0.25wt% ADS – 92.2%



O/M effects on sintering

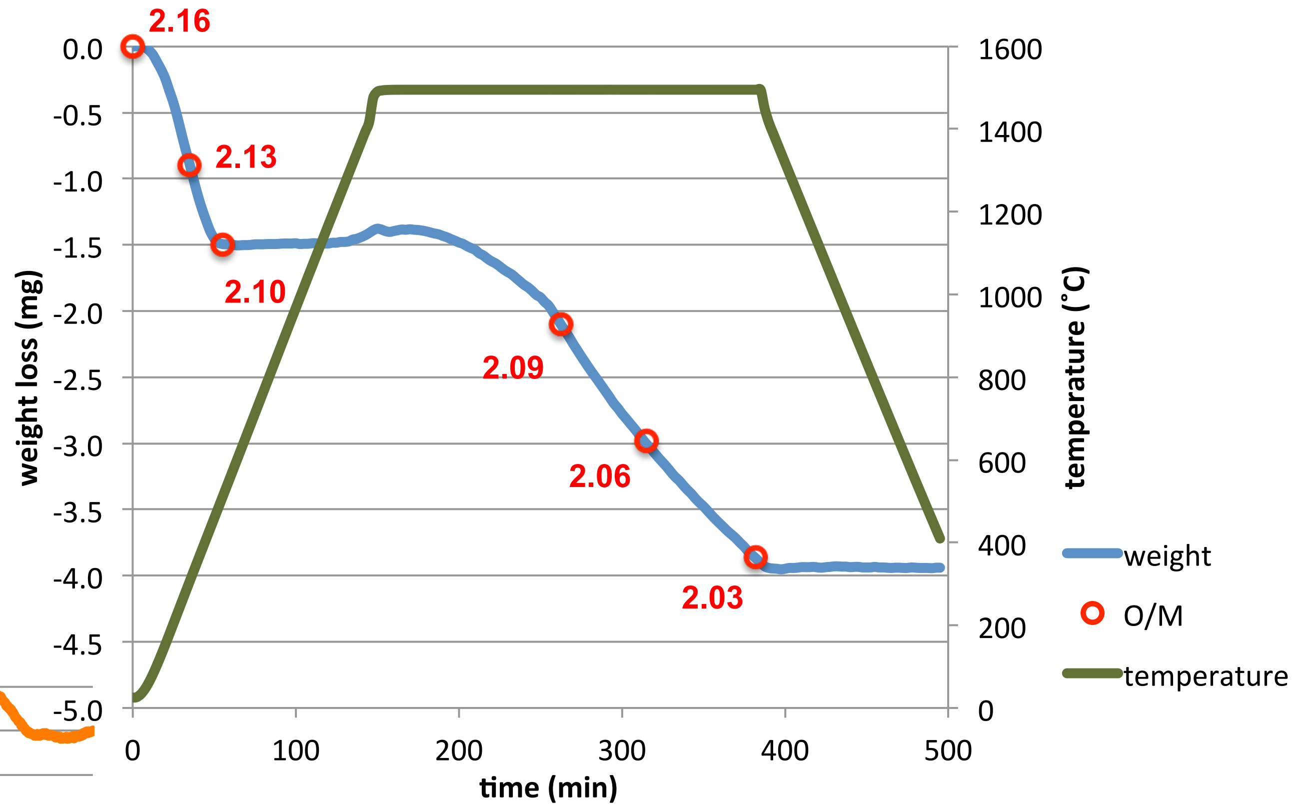
- UO_2 sintering is enhanced by hyperstoichiometry (O/U >2.00)
- Can adjust O/M of powder prior to processing or adjust with atmosphere

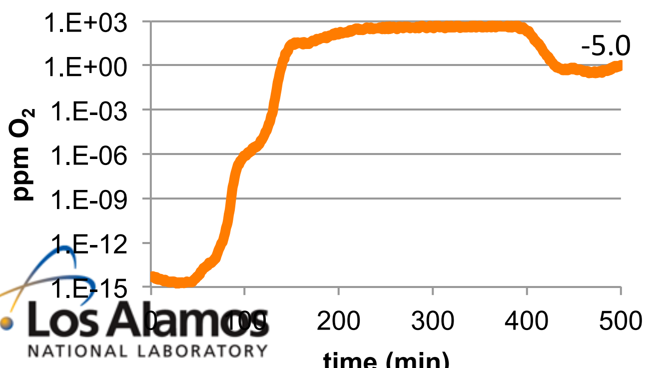




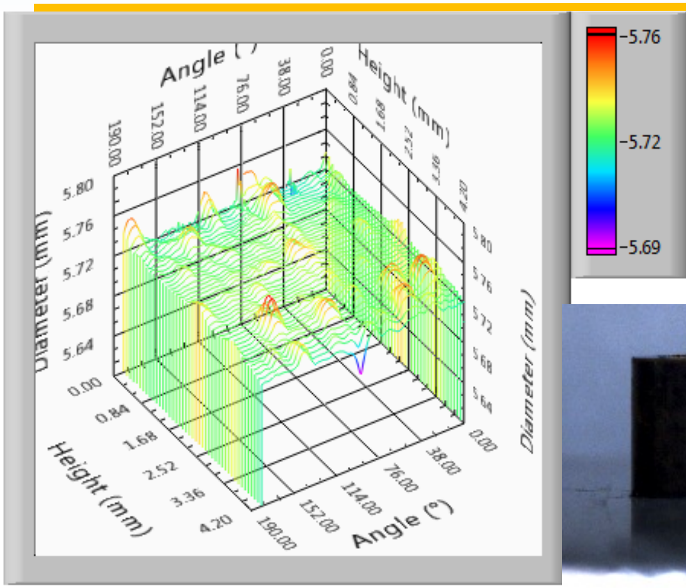
O/M control

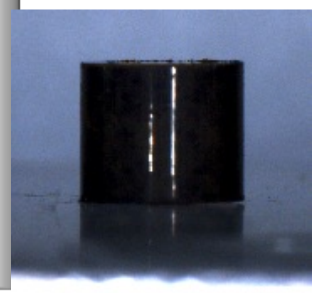
- Guided by thermodynamic modeling at ORNL
- Achieved with sophisticated gas control system
- Argon carrier with sub ppm hydrogen and oxygen control
- Allows precise sintering control



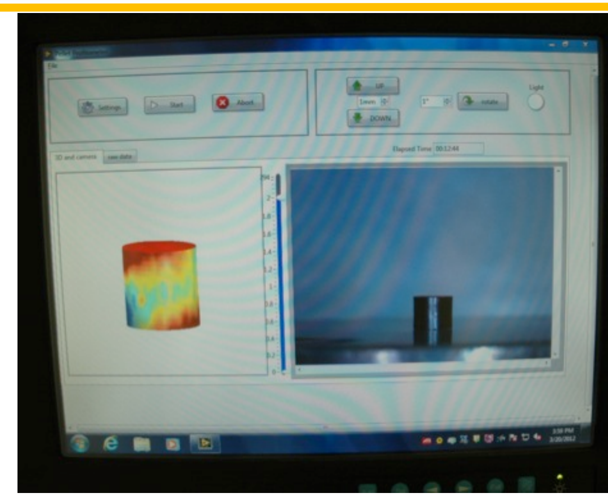


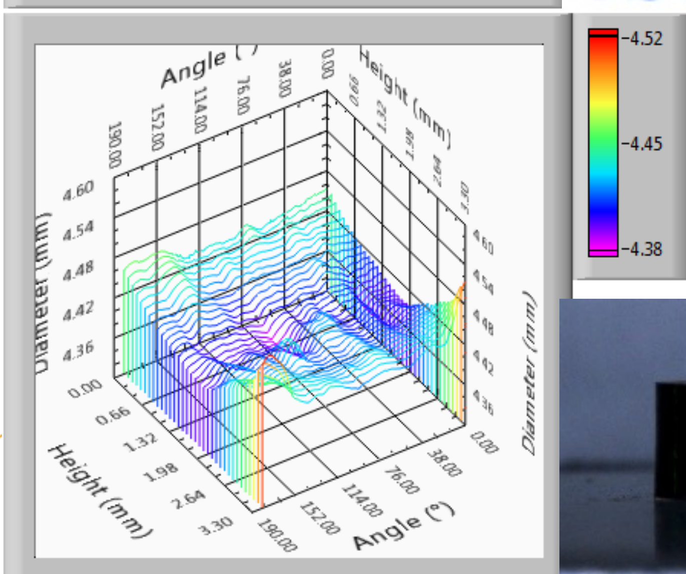
Dimensional changes due to sintering

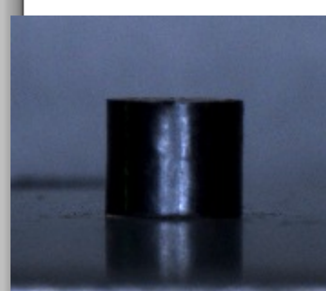




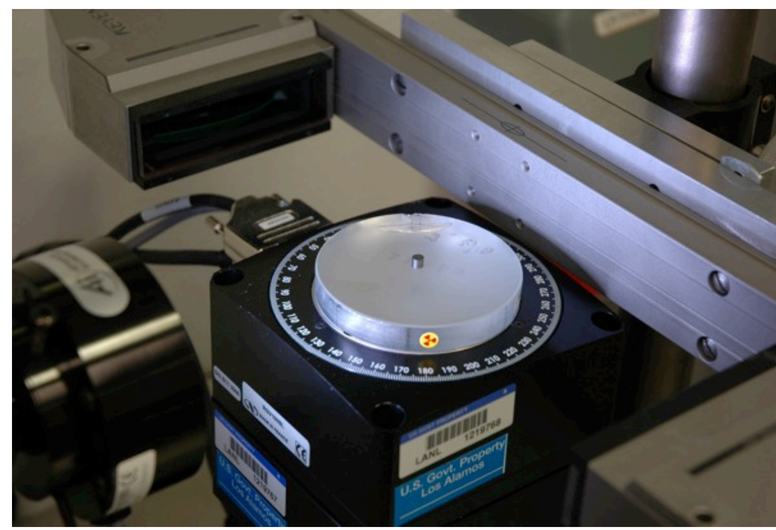
Green pellet shows uniform diameter







Sintered pellet shows “hourglassing”

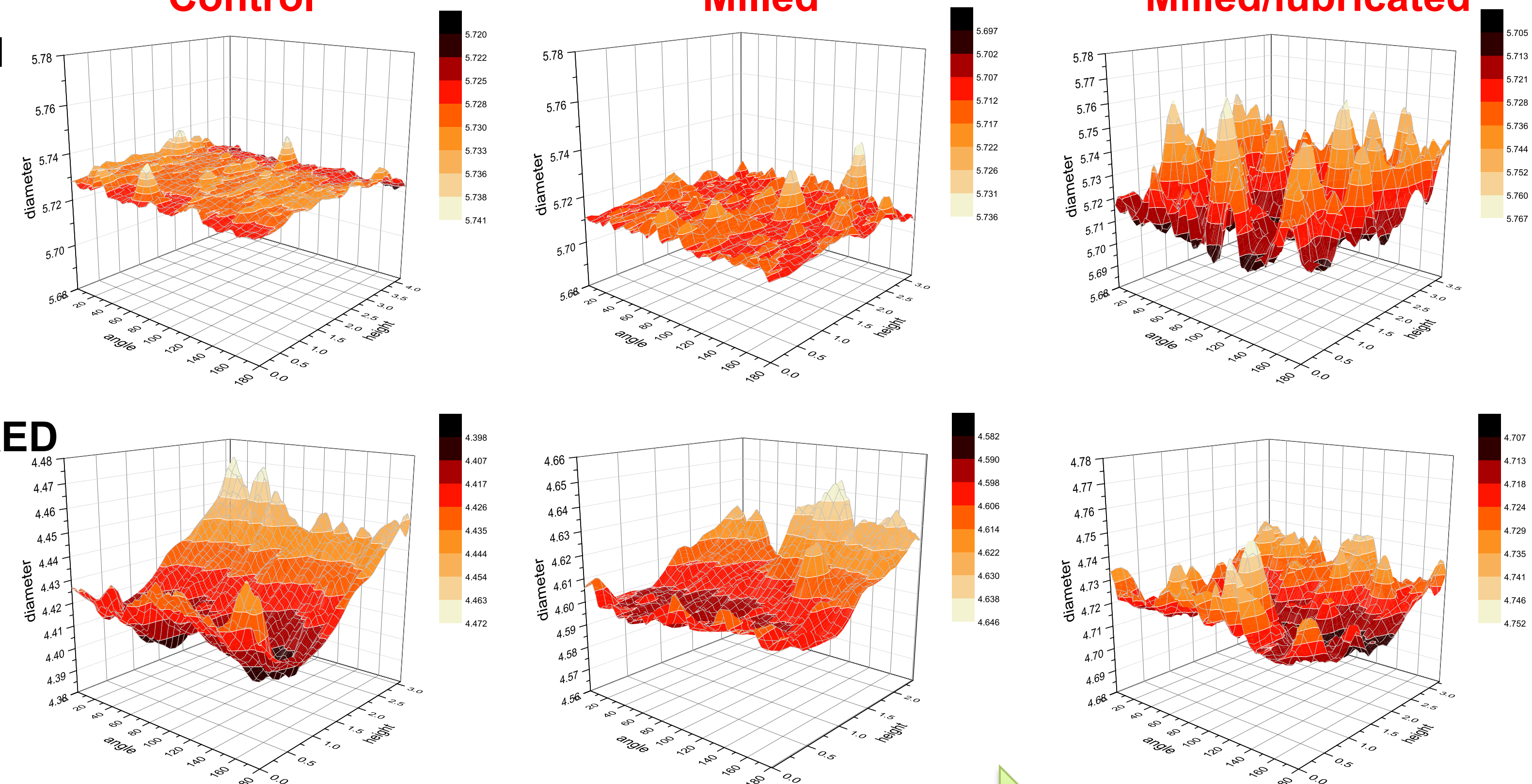


Processing modifications to minimize hourglassing

	Control	Milled	Milled/lubricated

GREEN pellets:

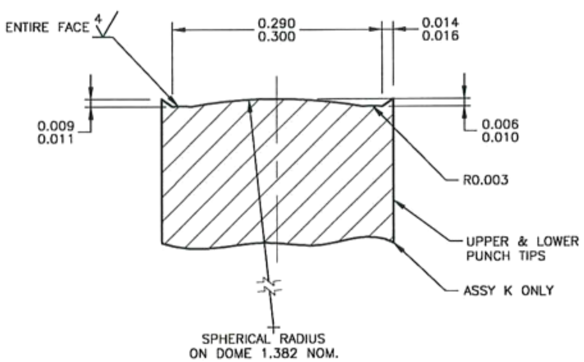
SINTERED Pellets:

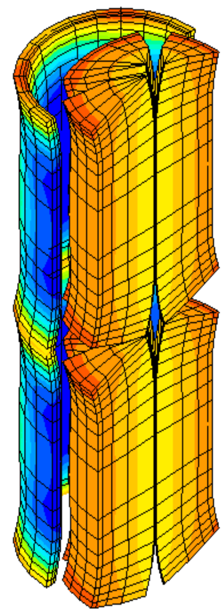


Less Hourglassing

Pellet Geometry

- **Dished and chamfered**
  - Dish to accommodate thermal expansion
  - Chamfer to minimize chipping
- **Why not barreled?**
- **Controlled porosity?**

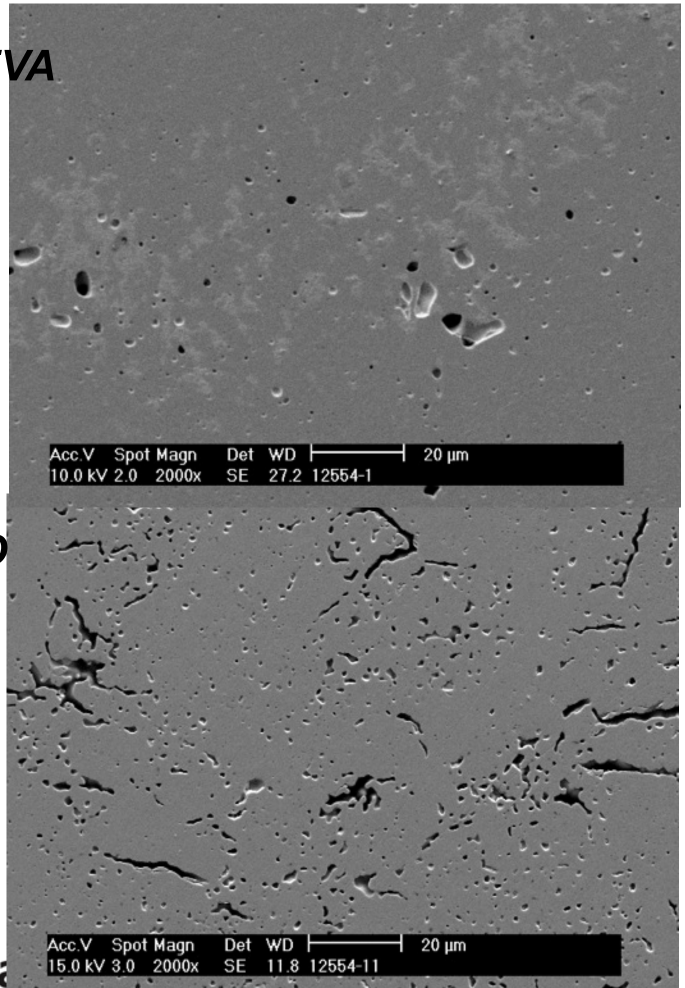


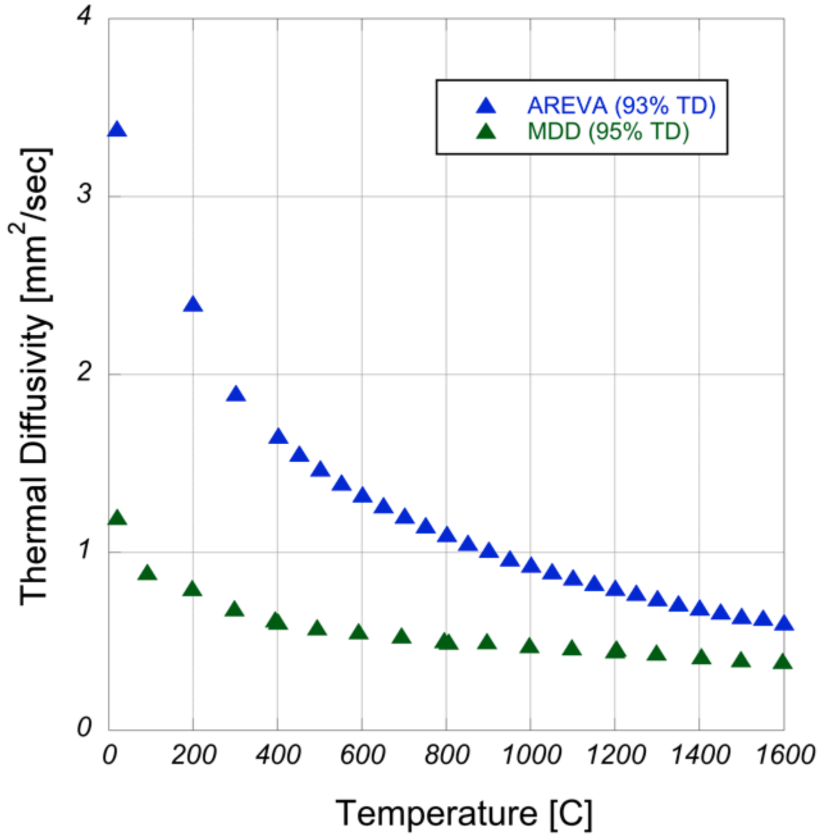


Microstructure Affects Properties
- Pore structure

AREVA

MDD



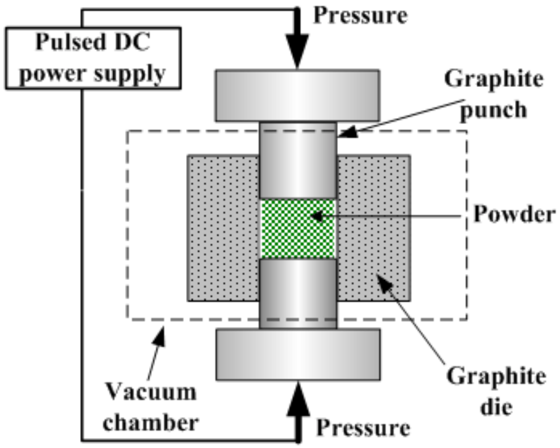


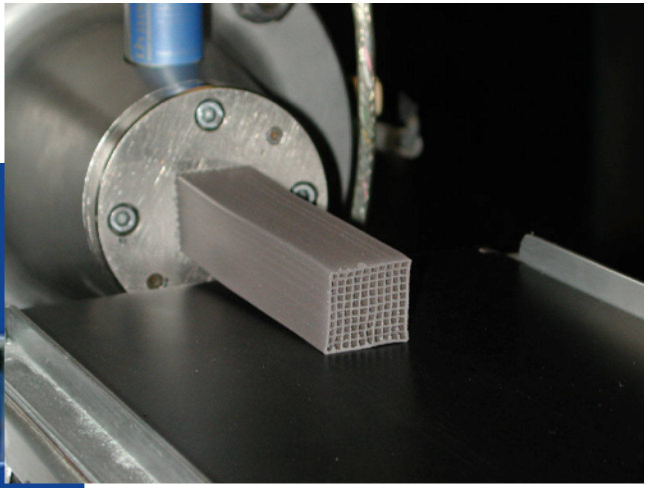
Diffusivity of MDD Pellet Compared to Typical Curve

Alternative Fabrication Methods

There's more than one way to skin a cat…

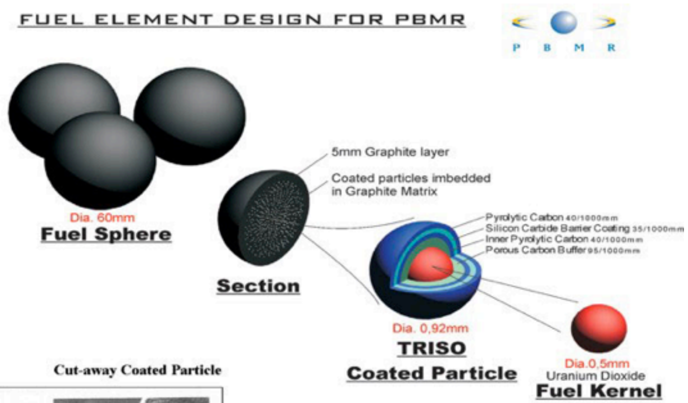
- **Spark Plasma Sintering (SPS)**
  - Rapid, near net shaping
  - Large volume production, microstructure
- **Extrusion**
  - Homogeneous microstructure, continuous, complex shapes
  - Liquid processing
- **Microwave sintering**
  - Rapid, remote equipment
  - Microstructure

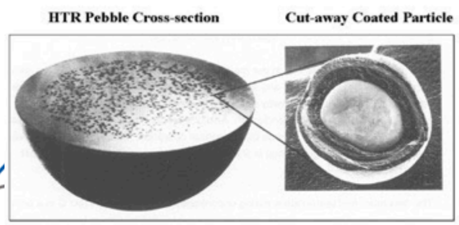


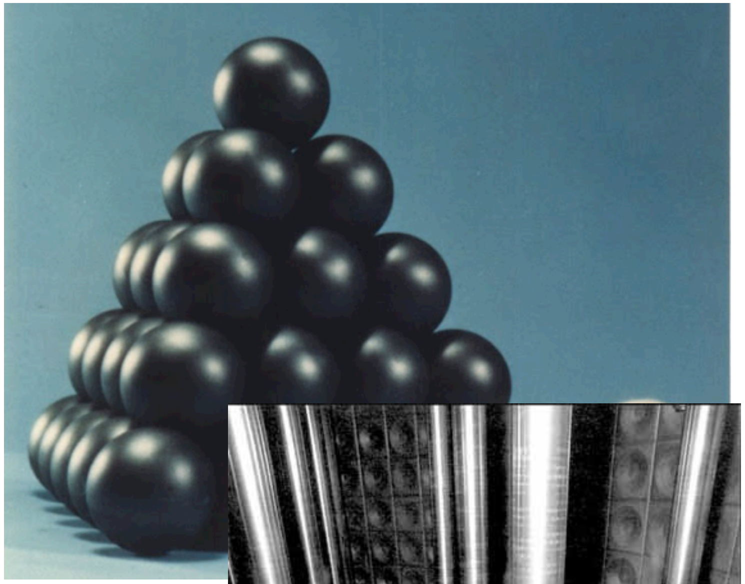


"Safer" designs

- High temp – crack steam to generate hydrogen
- 1/30th powder density
- Helium coolant
- Negative feedback stabilizes core around 1600C







Summary

- **Uranium oxide fuel pellets widely used in PWR, BWR, PHWR, AGR**
- **Fabrication by traditional cold press and sinter**
  - Powder conditioning
  - Compaction
  - Sintering
- **Properties of pellet are path dependent**
- **Most failure attributed to “missing pellet surface”**
- **Specifications, QC and process control**
- **Advanced characterization (EBSD, laser flash, 3D SEM)**
- **Alternative fabrication methods**

Acknowledgments

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ASU

Pedro Peralta

Perspective

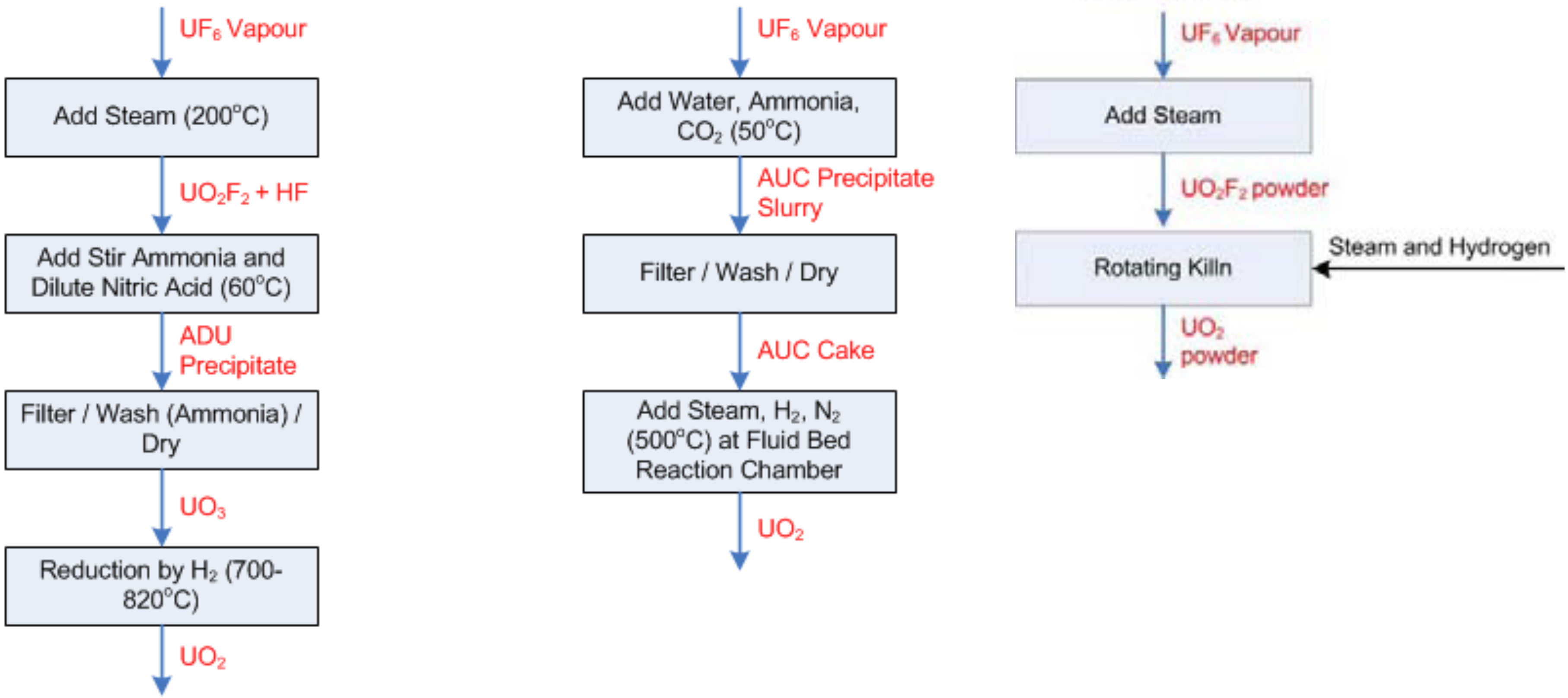
- **All the used nuclear fuel produced by the U.S. in 50 years of operation —approximately 62,500 metric tons—would only cover a football field to a depth of about 7 yards. –** Nuclear Energy Institute 2010
- **A 1000 MW(e) nuclear power station – produces ~ 30 tons of high level waste per year. In comparison, a 1000 MW(e) coal plant produces 300,000 tons of ash per year. –** International Atomic Energy Agency
- **Some coal deposits contain uranium at concentrations greater than 100 ppm. Burning coal concentrates this by a factor of ten.**
- **The fly ash emitted by a coal power plant carries into the surrounding environment 100 times more radiation than a nuclear power plant producing the same amount of energy. –** Scientific American
- **One fuel pellet provides as much energy as 1 ton of coal, 149 gallons of oil, 17,000 ft^3 of natural gas –** Ameren

UO_2 Reconversion Process

ADU Reconversion Process

AUC Reconversion Process

Integrated Dry Route (IDR)

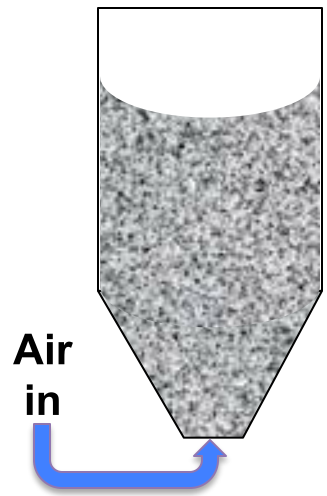


– Nuclear Fuel Cycle Information System, IAEA 2009

Everything you ever wanted to know about hoppers…*

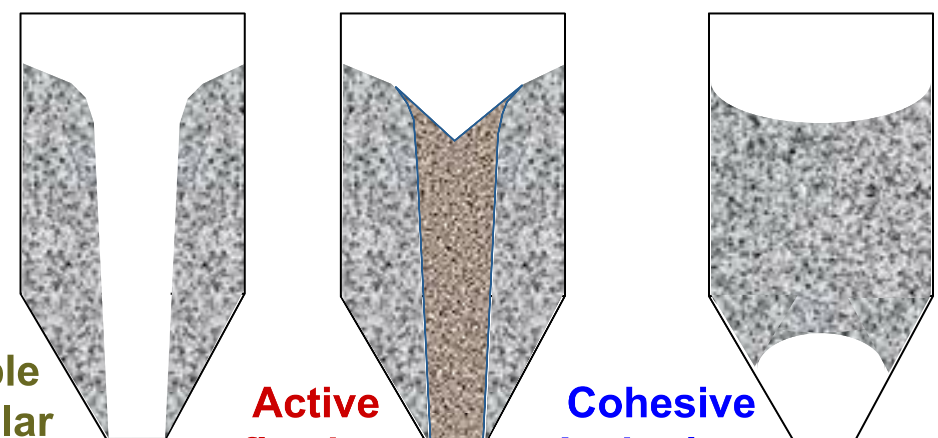
*but were afraid to ask

image from stellar manufacturing



Issues

- Ratholing/Piping
- Funnel Flow
- Arching/Doming
- Insufficient Flow
- Segregation
- Flushing



Stable annular region

Active flowing region

Cohesive Arch plugs hopper

Sintering Reality

- **Sintering**
  - Elemental diffusion
  - Impurities and/or sintering aids
  - Heat transport
  - O/M ratio
- **Small, high surface area, uniformly packed, “active” particles**
- **Processing space**
  - Powder conditioning
    - Milling, sieving, O/M, etc.
  - Pressing conditions
    - Density, density variations, etc.
  - Atmosphere (O/M)
    - Hydrogen, oxygen, water
    - Initial reduction, post reduction, constant O/M
  - Temperature and time

How do you grow grains?

How do you prevent grains from growing?

O/M controlled sintering

- Sintering a pellet under controlled atmosphere
- Complex P_{O2} profile to maintain constant O/M
- Guided by thermodynamic modeling at ORNL
- Achieved with sophisticated gas control system
- Argon carrier with sub ppm hydrogen and oxygen control